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Control and treatment of sulfur compounds specially sulfur oxides (SO_x) emissions from the petroleum industry: A review

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ABSTRACT

Sulfur compounds such as sulfur oxides (SO_x) are generated and emitted from operations in the petroleum industry which have negative effects on the environment. This study gives a critical and detailed introduction to the control and treatment of sulfur compounds specially sulfur oxides (SO_x) emissions from the petroleum industry. It begins with the sectors, main sources, and type of operations that generate SO_x emissions; maximum effluent level of them from the petroleum industry; minimization, control, prevention and treatment techniques of these emissions from the petroleum industry. Among these techniques, sulfur recovery unit (SRU) which most often consists of a Claus process for bulk sulfur removal and subsequently a tail gas treatment unit (TGTU) for the remaining H_2S removal (SCOT process, Beavon sulfur removal (BSR) process, and Wellman-Lord process) and flue-gas desulfurization (FGD) processes (once-through or regenerable) have been discussed in detail; and removal efficiencies and technical and economic aspects have been compared.

Capsule Summary: In present study the minimization, control, prevention and treatment techniques of sulfur compounds such as sulfur oxides (SOx) emissions from the petroleum industry is discussed.

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INTRODUCTION

The word "petroleum" means "rock oil" which is derived from the Latin petra (rock) and oleum (oil). The Latin word petra and oleum are loanwords from Greek πέτρα and ἔλαιον, respectively (Hyne, 2001, Organization of the petroleum exporting countries (OPEC), 2013). It refers to crude oil and natural gas.

Crude oil consists of approximately 10-14 wt % hydrogen and 83-87 wt % of carbon. Oxygen (0.05-1.5 wt %), sulfur (0.05-6 wt %), nitrogen (0.1-2 wt %), and metals such as vanadium, nickel, iron, and copper (nickel and vanadium < 1000 ppm) may be found as impurities in crude oil. Crude oil is not a uniform material and its exact molecular and fractional composition varies widely with formation of oil, location, age of the oil field, and the depth of the individual well. Crude oils obtained from different oil reservoirs have widely different characteristics (Speight, 1999, Verşan Kök, 2015).

An oil well produces predominantly crude oil, with some natural gas dissolved in it. But, a gas well produces predominantly natural gas. Natural gas consists of approximately 65-80% carbon, 1-25% hydrogen, 0-0.2% sulfur, and 1-15% nitrogen. Hydrocarbon molecules of natural gas generally are paraffin type that range from one to four carbon atoms in length, but up to six carbon atoms may also be found in small quantities. A typical natural gas

hydrocarbon composition is 70-98% methane, 1-10% ethane, trace to 5% propane, trace to 2% butane, and trace to 5% pentane and higher molecular weight hydrocarbons, including benzene and toluene (Hyne, 2001, Speight, 1999). In addition, water vapor, hydrogen sulfide (H_2S), carbon dioxide, helium, nitrogen, and other compounds in the minority may be found in raw natural gas (Devold, 2013). Gaseous impurities in natural gas that don't burn are called inert (noncombustible). Carbon dioxide, water vapor, helium and nitrogen are the major inert components in natural gas (Speight, 1999, Hyne, 2001).

Petroleum is vital to many industries, and is of importance to the maintenance of industrial civilization in its current configuration, and thus is a critical concern for many nations and petroleum accounts for a large percentage of the world's energy consumption (Jafarinejad, 2014a, 2014b, 2015a, 2015b, 2015c).

A wide variety of air pollutants such as nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), volatile organic compounds (VOCs), dust or particulates, etc. are generated and emitted from operations in the petroleum industry (E&P Forum, 1993, U.S. EPA, 1995, European Commission and Joint Research Center, 2013, Jafarinejad, 2015d). Intensification of the greenhouse effect associated with the global warming and climate change, acid rain, photochemical smog, reduced atmospheric visibility, death of forests, ozone depletion (from fire fighting agents), soot/heavy metals deposition, poorer water quality, surface water/groundwater contamination, soil contamination, disturbance of communities/flora/fauna, and destruction of ecosystem can be the environmental impacts of the petroleum industry (E&P Forum/UNEP, 1997, Speight, 2005, Mariano and La Rovere, 2007, Orszulik, 2008, Isah, 2012, Jafarinejad, 2015d). As sulfur compounds such as sulfur oxides (SO_x) are generated and emitted from operations in the petroleum industry and have negative effects on environment; in this study, the control and treatment methods of these emissions from the petroleum industry have been reviewed.

Petroleum industry and sulfur oxides (SO_x) emission sources

The petroleum industry includes the global processes of exploration, extraction, refining, transporting (pipeline, oil tanker/barge, truck, and rail), and marketing petroleum products. The industry is usually divided into three major components: upstream, midstream, and downstream. Upstream usually includes exploration, development, and production of crude oil and natural gas. Midstream segment, as its name implies, encompasses facilities and processes that sit between upstream and downstream segments. Midstream activities can include processing, storage and transportation of crude oils and natural gas. Transportation is a big part of midstream activities and can include using pipelines, trucking fleets, tanker ships, and rail cars. Downstream usually includes refining/hydrocarbon processing, marketing, and distribution. In another classification, the petroleum industry is divided into five segments upstream, downstream, pipeline, marine, and service and supply (EPA office of Compliance Sector Notebook Project, 2000, E.A. Technique (M) Berhad, 2014, EKT Interactive, 2015, Devold, 2013, Macini and Mesini, 2011). Thus, based on these classifications and discussion, the petroleum industry can be divided into four sectors: 1) exploration, development and production, 2) hydrocarbon processing (refineries and petrochemical plants), 3) storage, transportation, and distribution, 4) retail or marketing. Petroleum industry includes activities to explore for, produce, transport worldwide, process, and market approximately 3.5 billion tons of crude oil and 2.5 giga m^3 of natural gas and their derivatives per year (Cholakov, 2009). The sectors, main sources, and type of operations that generate sulfur oxides (SO_x) emissions have been given in Table 1.

Overview of control and treatment of sulfur oxides (SO_x) emissions

There are a variety of techniques for minimizing, controlling, preventing and treating sulfur oxides (SO_x) emissions to air that are listed below:

- Use of low-sulfur crude
- Liquid fuel desulfurization (hydrogenation reactions are taken place by hydrotreatment process and lead to reducing sulfur content)
- Treatment of refinery fuel gas (RFG), e.g. by acid gas removal to remove H_2S
- Use of gas such as on-site liquefied petroleum gas (LPG) or RFG or externally supplied gaseous fuel (e.g. natural gas) with a low level of sulfur and other undesirable substances to replace liquid fuel
- Use of SO_x reducing catalysts additives (note that SO_x reducing catalysts additives might have a detrimental effect on dust emissions by increasing catalyst losses due to attrition, and on NO_x emissions by participating in CO promotion, together with the oxidation of SO_2 to SO_3)
- Use of hydrotreatment process that reduces sulfur, nitrogen and metal content of the feed
- Acid gas (mainly H_2S) removal from the fuel gases, e.g. by amine treating (absorption)
- Use of sulfur recovery unit
- Use of tail gas treatment unit (TGTU)
- Use of flue-gas desulfurization (FGD) (European Commission and Joint Research Center, 2013); and
- Use of scrubbing systems (wet scrubbing, and dry or semi-dry scrubbing in combination with a filtration system) (Joseph and Beachler, 1998, Boamah et al., 2012, European Commission and Joint Research Center, 2013).

In this study, SRU which most often consists of a Claus process for bulk sulfur removal and subsequently a TGTU for the remaining H_2S removal (SCOT process, Beavon sulfur removal (BSR) process, and Wellman-Lord process) and FGD

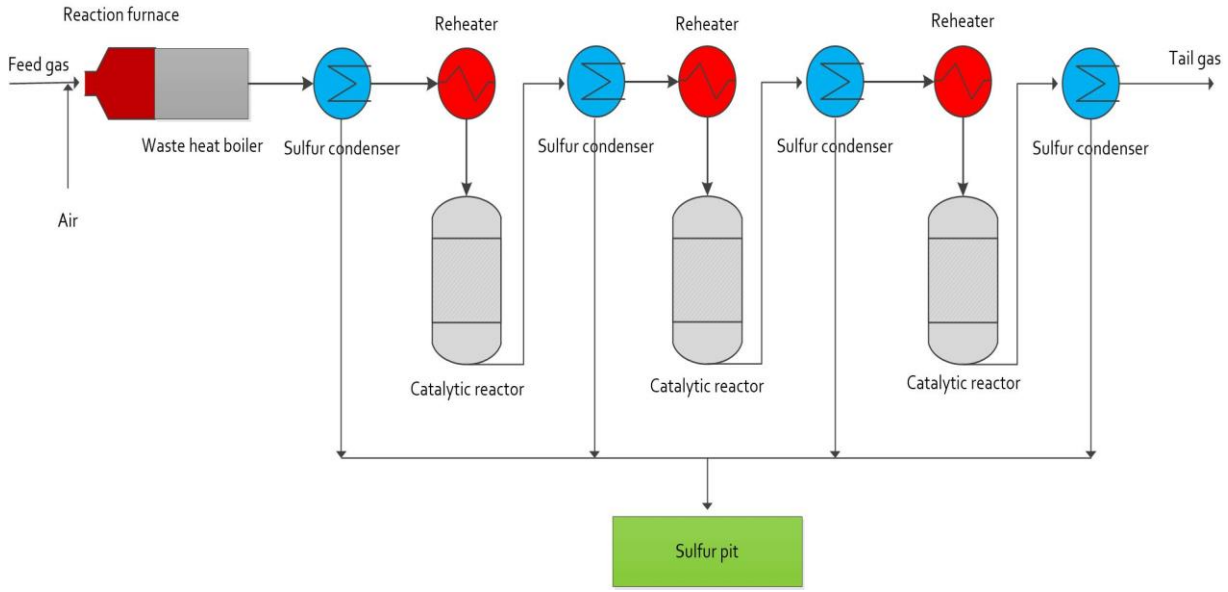

Fig. 1: A typical Claus process

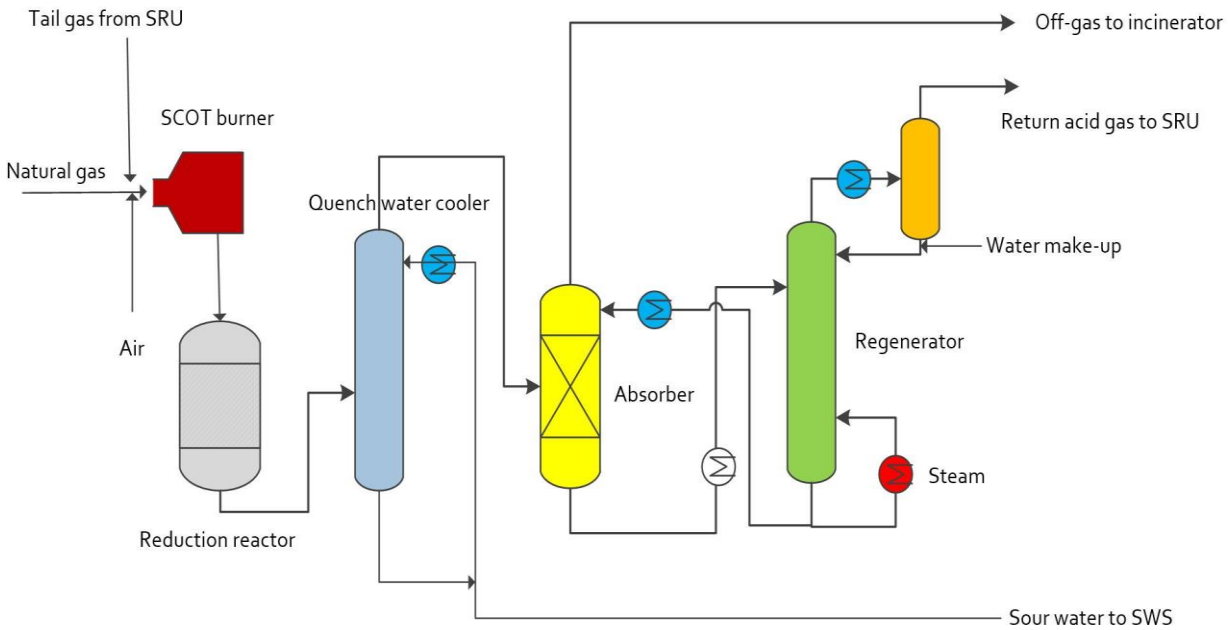

Fig. 2: Simplified process flow diagram of SCOT process (modified of European Commission and Joint Research Center, 2013)

processes (once-through or regenerable) have been discussed in detail.

According to World Bank Group (1998), some of the air emissions levels which should be achieved, have been presented in Table 2. Air emissions from stacks should be monitored once every shift, if not continuously, for opacity (maximum level, 10%). Air emissions of H_2S from a SRU should be monitored on a continuous basis. Annual emissions monitoring of combustion sources should be carried out for SO_x (sulfur content of the fuel monitored on a supply-tank basis) and for NO_x (World Bank Group, 1998).

Sulfur recovery unit (SRU)

The conversion of hydrogen sulfide (H_2S) to elemental sulfur is called sulfur recovery (U.S. EPA, 2015). SRU is an essential processing step to allow the overall facility to operate as the discharge of sulfur compounds to the atmosphere is severely restricted by environmental regulations (Street and Rameshni, 2011). H_2S-rich gas streams from amine-treating units and sour water strippers (SWS) are treated in a SRU, which most often consists of a Claus process for bulk sulfur removal and subsequently a TGTU for the remaining H_2S removal. Other components entering the SRU may include

Table 1: Main sources of sulfur oxides (SO_x) emissions from the petroleum industry

Sector	Sources	Type of operation
Exploration, development and production	Vent gases	Drilling
	Flare gases	Production
	Blowdown from bulk chemicals	
	Engine exhausts	Seismic
		Construction commissioning
		Drilling
		Production
		Maintenance
		Abandonment
Hydrocarbon processing (refineries)	Process furnaces and boilers, fluidized catalytic cracking regenerators, CO boilers, sulfur recovery units (SRU), flare systems, incinerators, or in processes such as crude oil desalting, atmospheric distillation, vacuum distillation, thermal cracking/visbreaking, coking, catalytic cracking, catalytic hydrocracking, hydrotreating/hydroprocessing, alkylation, isomerization, catalytic reforming, and propane deasphalting	
Hydrocarbon processing (petrochemical plants)	Furnaces, steam boilers, incinerators and flares, cracker unit, aromatic unit, and process heaters	

(E&P Forum, 1993, Bashat, 2003, U.S. EPA, 1995, Speight, 2005, European Commission and Joint Research Center, 2013, Department of Environment (DOE) of Malaysia, 2014, Iranian Ministry of Petroleum, 2007, IL & FS Ecosmart Limited Hyderabad, 2010, Jafarinejad, 2015d)

NH_3, CO_2 and, to a minor extent, various hydrocarbons (European Commission and Joint Research Center, 2013).

Claus process: The basic Claus unit consists of a thermal stage and two or three catalytic stages (Street and Rameshni, 2011). Fig. 1 shows a typical Claus process. It consists of a reaction furnace followed by a series of catalytic stages that each catalytic stage comprises a gas reheater, a catalyst chamber, and a condenser (European Commission and Joint Research Center, 2013, U.S. EPA, 2015). The process includes multistage catalytic oxidation of H_2S according to the following overall reaction (U.S. EPA, 2015):

$$2H_2S + O_2 \leftrightarrow 2S + 2H_2O \quad (1)$$

The furnace usually operates at higher temperatures ranging from 980 to 1540°C (U.S. EPA, 2015) or 1000 to 1400°C (Speight, 2005) with pressures rarely higher than 70 kilopascals (kPa) and one-third of the H_2S is burned with air in it to form sulfur dioxide according to the following reaction:

$$2H_2S + 3O_2 \leftrightarrow 2SO_2 + 2H_2O + heat \quad (2)$$

Before entering a sulfur condenser, hot gas from the combustion chamber is quenched in a waste heat boiler that generates high to medium pressure steam. About 80 percent of the heat released could be recovered as useful energy (U.S. EPA, 2015).

The catalytic reactors operate at lower temperatures, ranging from 200 to 315°C (U.S. EPA, 2015) or 200 to 350 (Speight, 2005) and the remaining uncombusted two-thirds of the H_2S reacts with SO_2 to form elemental sulfur as follows:

$$2H_2S + SO_2 \leftrightarrow 3S + 2H_2O + heat \quad (3)$$

Liquid elementary sulfur is collected from the various condensers in a covered pit. Alumina or bauxite can be used as a catalyst (U.S. EPA, 2015). Feed/air ratio control, temperature control of the furnace, reactors and condensers and good demisting of liquid sulfur, especially from the final condenser exit gas stream are important parameters in achieving maximum sulfur recovery (European Commission and Joint Research Center, 2013). Typical sulfur recovery efficiencies are in the range 95 to 97 (U.S. EPA, 2015) or 94 to 98 (European Commission and Joint Research Center, 2013) or 95 to 98% (Street and Rameshni, 2011) depending upon

the feed gas composition, number of catalytic reaction stages, the type of reheating method used (auxiliary burners or heat exchangers, with steam reheat for a natural gas processing plant and 3536 to 4223 kPa steam for a crude oil refinery) and generally plant configuration (Street and Rameshni, 2011, U.S. EPA, 2015). The tail gas containing H_2S, SO_2, sulfur vapor, traces of other sulfur compounds formed in the combustion section, and the inert gases from the condenser of the final catalytic stage is frequently entered a TGTU to recover additional sulfur and subsequently achieve higher recovery (U.S. EPA, 2015). Addition to TGTU, the SNO_x (a combined NO_x and SO_x abatement technique) or scrubber techniques may be used for this purpose (European Commission and Joint Research Center, 2013).

Many other side reactions also occur that produce carbonyl sulfide (COS) and carbon disulfide (CS_2), which have raised problems in many Claus plant operations because they cannot be easily converted to elemental sulfur and carbon dioxide (European Commission and Joint Research Center, 2013). Several of these possible side reactions are (U.S. EPA, 2015):

$$H_2S + CO_2 \rightarrow COS + H_2O \quad (4)$$

$$COS + H_2S \rightarrow CS_2 + 2H_2O \quad (5)$$

$$2COS \rightarrow CO_2 + CS_2 \quad (6)$$

The use of oxygen enrichment technologies (e.g OxyClaus process) can increase the overall capacity of the Claus plants; however, it does not increase sulfur recovery efficiency of these plants. An improved unique burner system and enhanced combustion conditions to reach a minimum temperature of 1350 °C, high-performance catalysts process (e.g. Selectox), and an automated control of the air feed are techniques that can be used and retrofitted to existing SRUs for increasing the Claus process efficiency (European Commission and Joint Research Center, 2013).

Tail gas treatment unit (TGTU): TGTU is a family of techniques which can be added to SRU in order to further removal and recovery of sulfur compounds. According to the principles applied, the most frequently operated TGTU processes can be broadly divided into the following four categories:

- Direct oxidation to sulfur (PRO-Claus stands for Parson RedOx Claus with expected sulfur recovery efficiency of 99.5% and the SUPERCLAUS process with expected sulfur recovery efficiency of 98-99.3%);
- Continuation of the Claus reaction (Cold Bed Absorption (CBA) process with expected sulfur recovery efficiency of 99.3-99.4%, the CLAUSPOL process with expected sulfur recovery efficiency of 99.5-99.9%, and the SULFREEN process (HYDROSULFREEN with expected sulfur recovery efficiency of 99.5-99.7%, DOXOSULFREEN with expected sulfur recovery efficiency of 99.8-99.9%, and MAXISULF with expected sulfur recovery efficiency of 98.5% (note that expected sulfur recovery efficiency for third stage Claus + MAXISULF process is 99-99.5%)));
- Reduction to H_2S and recovering sulfur from this H_2S (The FLEXSORB process with expected sulfur recovery efficiency of 99.9%, High Claus Ratio (HCR) process, Reduction, Absorption, Recycle (RAR) process with expected sulfur recovery efficiency of 99.9%, the SCOT process (H_2S scrubbing) with expected sulfur recovery efficiency of 99.5-99.95% for amine based process, and the Beavon Sulfur Removal (BSR) process with expected sulfur recovery efficiency of 99.5-99.9%) (European Commission and Joint Research Center, 2013) ; and
- Oxidation to SO_2 and recovering sulfur from SO_2 (the Wellman-Lord process with expected sulfur recovery efficiency of 99.9%,, the CLINTOX process, and the LABSORB process) (European Commission and Joint Research Center, 2013, U.S. EPA, 2015).

Among these processes, SCOT process, BSR process, and Wellman-Lord process are often used to recover additional sulfur; which are described in this section.

SCOT process: The SCOT process is widely applied to recover sulfur from the Claus tail gas (Speight, 2005, European Commission and Joint Research Center, 2013, U.S. EPA, 2015). Fig. 2 shows the simplified process flow diagram (PFD) of SCOT process. In this type of scrubbing process, sulfur in the tail gas is converted to H_2S using hydrogenation and hydrolysis of all sulfur compounds by passing it through a cobalt-molybdenum catalyst at 300 °C with the addition of a reducing gas. The gas is then cooled and sent to a absorber, where H_2S is absorbed by an amine solution (generic amine or specialty amine). The sulfide-rich amine solution is sent to a regenerator, where H_2S is removed and recycled to the upfront Claus reaction furnace. The amine solution is regenerated and returned to the absorber (European Commission and Joint Research Center, 2013).

Beavon sulfur removal (BSR) process: The BSR process is used to recover sulfur from the Claus tail gas (Street and Rameshni, 2011, U.S. EPA, 2015) and this process can represent Best Available Control Technology (BACT), potentially achieving 99.99+% overall sulfur recovery with emissions of < 10 ppmv H_2S and 30 ppmv total sulfur (Rameshni). It can also be effective in removing small amounts of SO_2, COS, and CS_2 that are not affected by the Claus process (Speight, 2005, Street and Rameshni, 2011). Fig. 3 shows a typical simplified BSR amine system scheme. This process has two steps. In the first step, all sulfur compounds are catalytically (cobalt-molybdate based) converted into H_2S through an hydrogenation/hydrolysis reaction at high temperature (300 – 400°C) (European Commission and Joint Research Center, 2013). In real, the Claus tail gas is heated approximately to 290-340°C by inline sub-stoichiometric combustion of natural gas in a reducing gas generator (RGG) (In the RGG, some reducing gas H_2 and CO are produced) for subsequent catalytic reduction of virtually all non-H_2S sulfur components to H_2S. Elemental

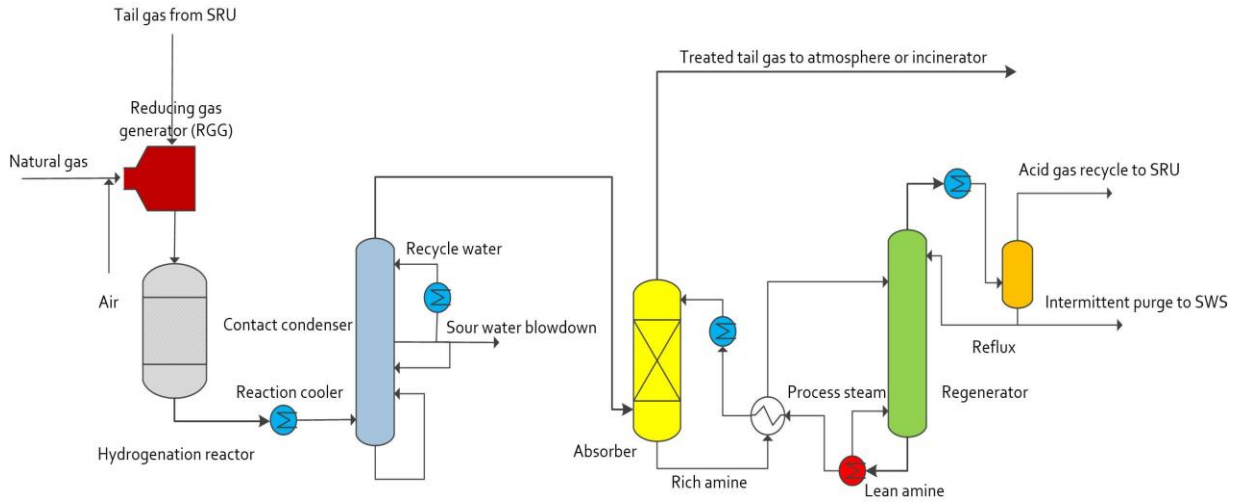

Fig. 3: A typical simplified BSR amine system scheme (modified of Street and Rameshni, 2011)

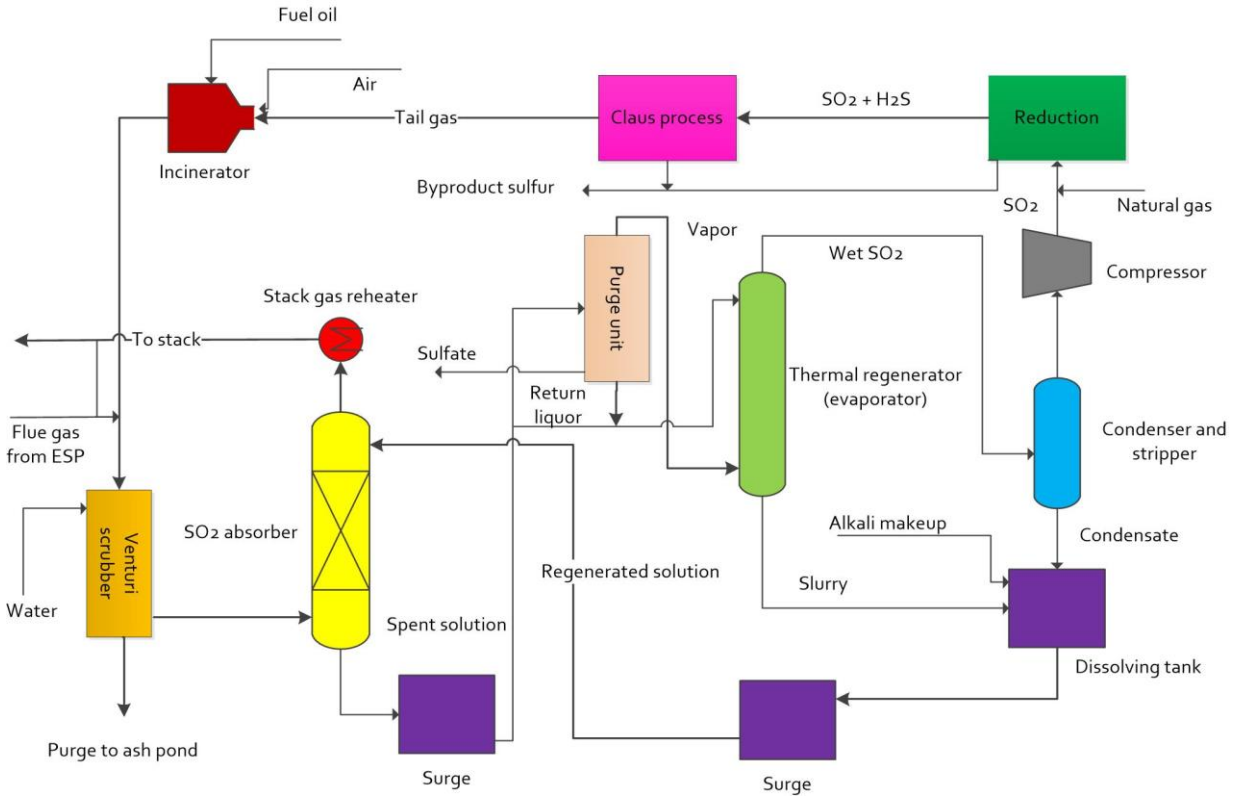

Fig. 4: Schematic process flow diagram of Wellman-Lord and Allied chemical process (modified of Tri-State Synfuels Company, 1982)

sulfur (S_x) and SO_2 are converted by hydrogenation in reactor according to the following reactions:

$$S_x + xH_2 \rightarrow xH_2S \quad (7)$$

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O \quad (8)$$

COS and CS_2 are converted by hydrolysis in reactor according to the following reactions:

$$COS + H_2O \rightarrow H_2S + CO_2 \quad (9)$$

$$CS_2 + 2H_2O \rightarrow 2H_2S + CO_2 \quad (10)$$

The reactions are exothermic and heat is removed from the gas in the reaction cooler, which produces steam. The gas is cooled further in a direct contact condenser (or quench tower) by a circulating water stream down to a suitable

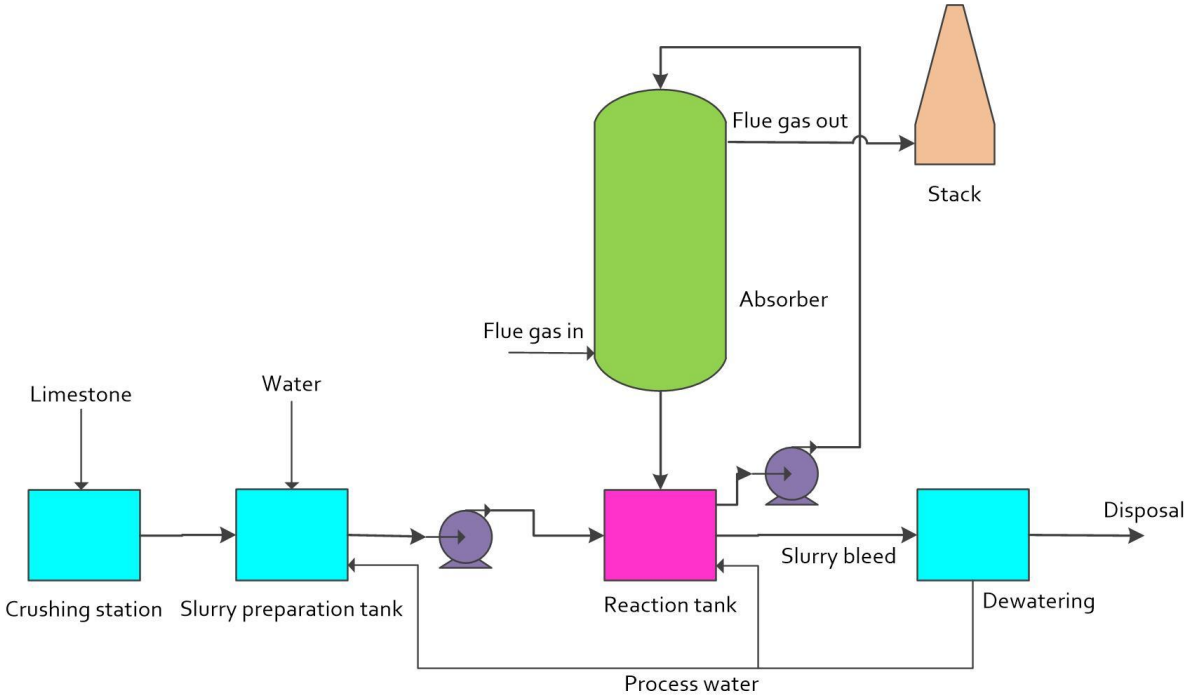

Fig. 5: A schematic PFD of a limestone-based wet FGD process (modified of Srivastava and Jozewicz, 2001)

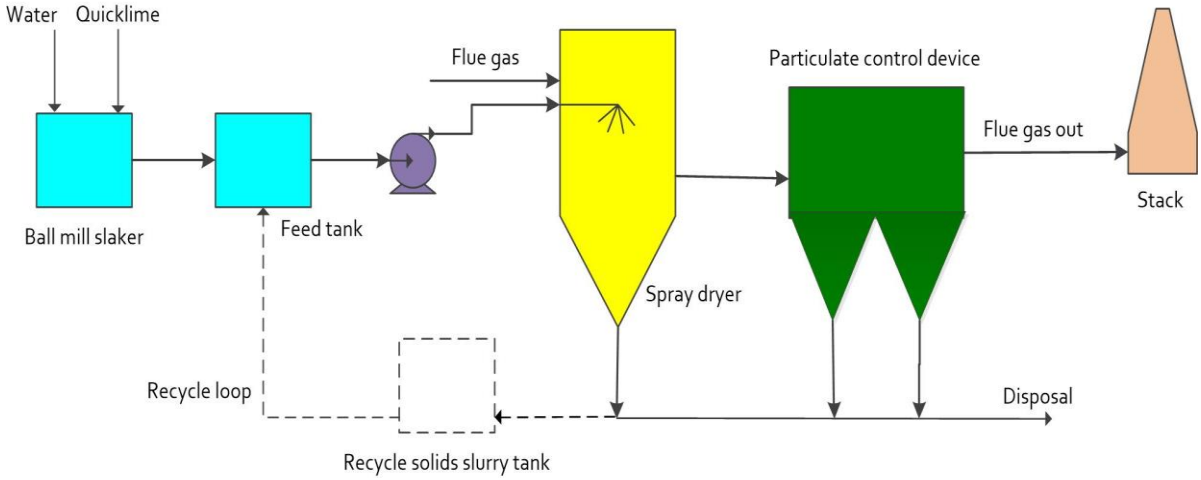

Fig. 6: The schematic of LSD process (modified of Srivastava and Jozewicz, 2001)

temperature for the second step and sour water is condensed from the stream (Street and Rameshni, 2011).

In the second step, generally, H_2S can be removed by a chemical solution (e.g. amine process) or another tail gas process (e.g. the Stretford redox process) (European Commission and Joint Research Center, 2013, Rameshni). In amine treatment process, gas is contacted with lean amine solution in the absorber, which the H_2S and some of the CO_2 are absorbed by the amine. The treated gas is sent to the thermal oxidizer where residual H_2S is converted to SO_2 before discharge to atmosphere. The rich amine is sent to the regenerator after being heated in the Lean/Rich exchanger by the hot lean amine from the bottom of the regenerator. In the regenerator, the acid gases are released from solution by heating the solution in the reboiler. The overhead from the regenerator is cooled and the condensate returned to the column. The cooled, water saturated, acid gas is recycled to the Claus Unit. The hot lean amine is cooled firstly by heating the rich solution and then in the lean amine cooler before entering the absorber (Street and Rameshni, 2011).

Wellman-Lord process: The Wellman-Lord process uses a wet generative process to reduce flue gas SO_2 concentration to less than 250 ppmv and can achieve approximately 99.9% sulfur recovery (U.S. EPA, 2015). This process is the most widely used regenerative process (European Commission and Joint Research Center, 2013) that incorporates the flue gas pretreatment, sulfur dioxide absorption, absorbent

regeneration, sulfate removal processes. After absorbent regeneration, the obtained SO_2 can be liquefied or used for successive production of sulfuric acid or sulfur, e.g. the so called Wellman-Lord and Allied chemical process (Atanasova et al., 2013). Fig. 4 shows the schematic PFD of Wellman-Lord and Allied chemical process. SRU tail gas is incinerated and all sulfur species are oxidized to form SO_2 in this process (U.S. EPA, 2015). Gases are then entered in a preliminary absorber (Venturi prescrubber) and cooled and quenched to remove excess water and to reduce gas temperature to absorber conditions and the most of the solid impurities, chlorides, part of the SO_2, etc. are captured (Tri-State Synfuels Company, 1982, Atanasova et al., 2013). The rich SO_2 gas is then reacted with a solution of sodium sulfite (Na_2SO_3) to form the bisulfite (Tri-State Synfuels Company, 1982, Atanasova et al., 2013, U.S. EPA, 2015):

$$SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3 \quad (11)$$

The offgas is reheated and vented to stack. The resulting bisulfite solution is boiled in an evaporator-crystallizer, where it decomposes to SO_2 and water (H_2O) vapor and sodium sulfite is precipitated:

$$2NaHSO_3 \rightarrow Na_2SO_3 \downarrow + H_2O + SO_2 \uparrow \quad (12)$$

Sulfite crystals are separated and redissolved for reuse as lean solution in the absorber (U.S. EPA, 2015). Sodium sulfite slurry produced from the evaporators is dissolved in stripped condensate which is derived from the evaporator overhead vapors. Sodium carbonate makeup is added to the dissolving tank to replace the sodium lost in the purge streams. The sodium carbonate reacts with sodium bisulfite in the dissolving tank to form additional sodium sulfite (Tri-State Synfuels Company, 1982):

$$Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + H_2O + CO_2 \quad (13)$$

The wet SO_2 gas is directed to a partial condenser where most of the water is condensed and reused to dissolve sulfite crystals. The enriched SO_2 stream is then recycled back and used for conversion to elemental sulfur or production of sulfuric acid (Atanasova et al., 2013, U.S EPA, 2015).

Production of pure SO_2 with no residuals and high capital investments for the plant construction are advantage and substantial disadvantage of Wellman-Lord process, respectively. The great amount of steam for regeneration of the solution is another drawback (Atanasova et al., 2013). According to Kolev (2000) and Atanasova et al. (2013), three solutions have been proposed for substantial reduction of the steam consumption of the method on the basis of a significant increase of the SO_2 concentration in the saturated absorbent and consequently enhancements of Wellman-Lord method:

- Additional saturation of the absorption solution with Na_2SO_3, after partial transformation of the initial Na_2SO_3 into $NaHSO_3$;
- Preliminary cooling of the flue gases in the packing beds of a contact economizer system and utilization of the waste heat of the gases for district heating water and for heating and humidifying of the air fed into the boiler combustor; and
- Development of new types of packings and liquid distributors.

Flue-gas desulfurization (FGD)

The FGD is a scrubbing technique which uses an alkaline reagent (typically a sodium or calcium based alkaline regent) to remove SO_2 from flue gas (Tri-State Synfuels Company, 1982, Tilly, 1983, Srivastava and Jozewicz, 2001, U.S. EPA, 2003, Ramadan, 2004, Dehghani and Bridjanian, 2010, European Commission and Joint Research Center, 2013). The reagent is injected in the flue gas in a spray tower and directly into the duct and absorb, neutralize and/or oxidize the SO_2. Thus, the solid sulfur compounds such as calcium sulfate (gypsum), sodium sulfate, etc. depending on alkaline reagent are made which are removed from the waste gas stream using downstream equipment (U.S. EPA, 2003).

FGD processes can be classified as once-through or regenerable, depending on how the sorbent is treated after it has sorbed SO_2 or how the generated solids by the process are handled (Srivastava and Jozewicz, 2001, U.S. EPA, 2003). In once-through technologies, the spent sorbent is disposed of as a waste or utilized as a byproduct. In regenerable technologies, SO_2 is released from the sorbent during the sorbent's regeneration, and the SO_2 may be further processed to yield H_2SO_4, elemental sulfur, or liquid SO_2. No waste is produced in regenerable technology applications (Srivastava and Jozewicz, 2001). Generally, regenerable processes have higher costs than once-through technologies; however, regenerable processes might be selected if space or disposal options are restricted and markets for byproducts are available (U.S. EPA, 2003).

Both once-through and regenerable technologies can be further classified as wet, semi-dry, or dry (U.S. EPA, 2003). Limestone forced oxidation (LSFO), limestone inhibited oxidation (LSIO), jet bubbling reactor (JBR), lime process, magnesium enhanced lime (MEL), dual alkali, and seawater process are examples of wet once-through technologies; whereas, lime spray drying (LSD), furnace sorbent injection (FSI), LIFAC process, economizer sorbent injection (ESI), duct sorbent injection (DSI), duct spray drying (DSD), circulating fluidized bed (CFB), and Hypas sorbent injection (HSI) are examples of semi-dry or dry once-through technologies. Besides, sodium sulfite process, magnesium oxide process, sodium carbonate process, and amine process are examples of wet regenerable technologies; whereas, activated carbon is an example of dry regenerable technologies (Srivastava and Jozewicz, 2001).

High SO_2 removal efficiencies from 50% up to 98%; probable reusable of reaction products; relatively simple retrofitting; and relatively lower price and availability of reagents are advantages of FGD technologies; whereas, high operation and maintenance (O&M) and capital costs; scaling and depositing of wet solids on absorber and downstream equipment; visible plume of wet systems; non-usability for waste gas SO_2 concentrations greater than 2000 ppm; and increase of O&M costs due to disposal of waste products are disadvantages of FGD technologies (U.S. EPA, 2003).

Wet FGD systems: In wet processes, flue gas is ducted to a spray tower where aqueous slurry of sorbent is injected from the nozzles into the flue gas. A portion of the water in the slurry is evaporated and the waste gas stream becomes saturated with water vapor. In the absorber, SO_2 dissolves in the slurry and initiates the reaction with dissolved alkaline particles. The slurry is collected at the bottom of the absorber and treated flue gas is passed through a mist eliminator to remove any entrained slurry droplets before exiting the absorber. The absorber bottom effluent is sent to a reaction tank to complete the SO_2-alkaline reaction and form a neutral salt. In an once-through system, the spent slurry is dewatered to disposal or use as a byproduct (Fig. 5); but, in a regenerable system, the spent slurry is recycled back to the absorber (U.S. EPA, 2003). Lime is easier to manage on-site and has control efficiencies up to 95% but is significantly more costly; whereas, limestone is very inexpensive but control efficiencies for limestone systems are limited to approximately 90%. There are special sorbents with reactivity enhancing additives which provides control efficiencies greater than 95% but are very costly. The volume ratio of reagent slurry to waste gas (L/G) determines the amount of reagent available for reaction with SO_2. Higher L/G can increase the control efficiency and decrease the formation of scale in the absorber due to oxidation of SO_2. This parameter is approximately 1:1 for wet scrubbers and is expressed as gallons of slurry/1000 ft^3 of flue gas (U.S. EPA, 2003).

Semi-dry FGD systems: In semi-dry systems or spray dryers, aqueous sorbent slurry similar to wet systems is injected; however, the slurry has a higher sorbent concentration. The hot flue gas is mixed with the slurry solution which causes water evaporation from the slurry. The remaining water on the solid sorbent enhances the reaction with SO_2. A dry waste product is generated which is collected with a standard PM collection device such as a baghouse or ESP. This product can be disposed, sold as a byproduct or recycled to the slurry (U.S. EPA, 2003).

Various calcium and sodium based reagents can be used as sorbent but lime is typically injected in spray dry scrubbers. The schematic of LSD is shown in Fig. 6. Rotary atomizers or two-fluid nozzles are utilized to finely disperse lime slurry into the flue gas. A close approach to adiabatic saturation (from 10 to 15 ºC for flue gas) is required to achieve high SO_2 removal. High SO_2 capture in the spray dryer occurs when the sorbent is still moist (U.S. EPA, 2003, Srivastava and Jozewicz, 2001). Lower L/G ratios approximately 1:3 should be used and flue gas with high SO_2 concentrations or temperatures can reduce the performance of the scrubber. Generally, SO_2 control efficiencies for spray dry scrubbers are between 80% and 90%. Large units may require multiple absorber systems. Carbon steel can be used to construct the absorber and the capital and operating costs for spray dry scrubbers are lower than for wet scrubbers (U.S. EPA, 2003).

Dry FGD systems: In dry systems, powdered sorbent is directly injected pneumatically into the furnace (temperature approximately between 950 and 1000 °C), the economizer (temperature approximately between 500 and 570 °C), or downstream ductwork (temperature approximately between 150 and 180 °C) by dry sorbent injection systems. Injection temperature and residence time are critical parameters for SO_2 removal. Injection needs suitable temperature conditions in order to decompose sorbent into porous solids with high surface area. A dry waste product is collected with a standard PM collection device such as a baghouse or ESP. The flue gas is generally cooled prior to the entering PM control device. To enhance SO_2 removal, water can be injected upstream of the absorber (U.S. EPA, 2003, Srivastava and Jozewicz, 2001). A schematic of once-through dry FGD processes involving dry powder injection and duct spray drying have been shown in Fig. 7. In this figure, the flue gas flow for a plant without FGD has been shown with the solid line. Sorbent injection locations for alternative dry FGD processes with dry powder injection or duct spray drying have been shown schematically with broken lines (Srivastava and Jozewicz, 2001). Various calcium and sodium based reagents and a number of proprietary reagents can be used as sorbent. SO_2 removal by the sorbent can be enhanced by injection of water downstream of the sorbent injection (U.S. EPA, 2003). The capital and annual costs for dry scrubbers are significantly lower than for wet scrubbers. Dry systems are installed easily

Table 2: Maximum effluent level from the petroleum industry (World Bank Group, 1998)

Parameter	Maximum value
Nitrogen oxides (mg/m^3) (Excludes NO_x emissions from catalytic units)	460
Sulfur oxides (mg/m^3)	150 for SRUs and 500 for other units.
Particulate matter (PM) (mg/m^3)	50
Nickel and vanadium (combined) (mg/m^3)	2
Hydrogen sulfide (mg/m^3)	152

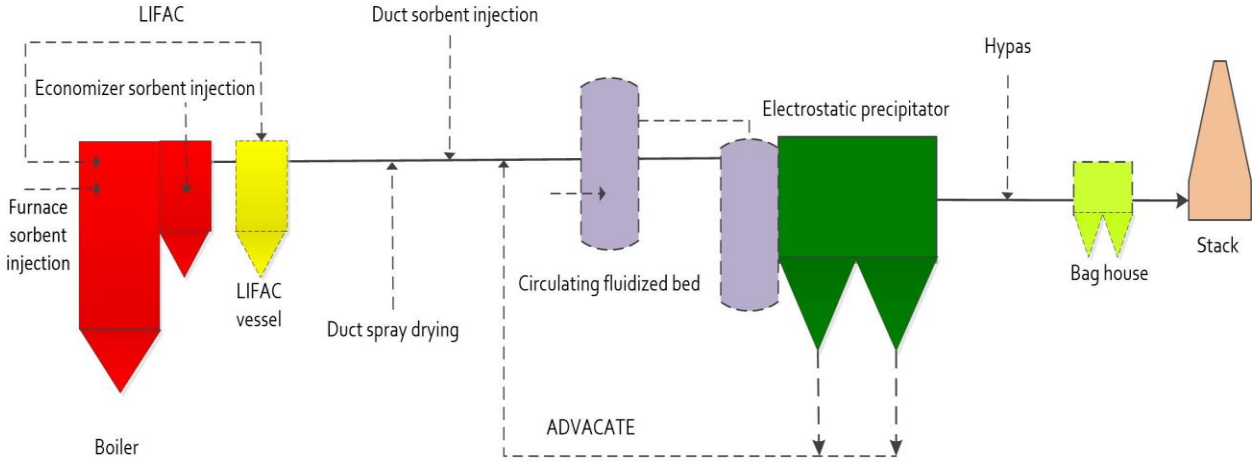

Fig. 7: A schematic of once-through dry FGD processes involving dry powder injection and duct spray drying (modified of Srivastava and Jozewicz, 2001)

and are good candidates for retrofit applications. SO_2 removal efficiencies are between 50% and 60% for calcium based sorbents and up to 80 % for sodium based sorbents injection into the duct (U.S. EPA, 2003, Srivastava and Jozewicz, 2001). Dry systems are good SO_2 control technologies for medium to small industrial boiler applications and newer designs of these systems for small industrial boilers have achieved greater than 90% SO_2 removal efficiencies (U.S. EPA, 2003).

CONCLUSIONS

In this study, the sectors, main sources, and type of operations that generate SO_x emissions; maximum effluent level of them from the petroleum industry; minimization, control, prevention and treatment techniques of these emissions from the petroleum industry have been reviewed. Among these techniques, SRU which most often consists of a Claus process for bulk sulfur removal and subsequently a tail gas treatment unit TGTU for the remaining H_2S removal (SCOT process, Beavon sulfur removal (BSR) process, and Wellman-Lord process) and FGD processes (once-through or regenerable) have been discussed in detail. In Claus process, typical sulfur recovery efficiencies are in the range 94 to 98% depending upon the feed gas composition, number of catalytic reaction stages, the type of reheating method used (auxiliary burners or heat exchangers, with steam reheat for a natural gas processing plant and 3536 to 4223 kPa steam for a crude oil refinery) and generally plant configuration. The expected sulfur recovery efficiency for the SCOT process (H_2S scrubbing) is in the range 99.5-99.95% for amine based process. BSR process can represent Best Available Control Technology, potentially achieving 99.99+% overall sulfur recovery with emissions of less than 10 ppmv H_2S and 30 ppmv total sulfur. The Wellman-Lord process uses a wet generative process to reduce flue gas SO_2 concentration to less than 250 ppmv and can achieve approximately 99.9% sulfur recovery. In this process, additional saturation of the absorption solution with Na_2SO_3, after partial transformation of the initial Na_2SO_3 into $NaHSO_3$; preliminary cooling of the flue gases in the packing beds of a contact economizer system and utilization of the waste heat of the gases for district heating water and for heating and humidifying of the air fed into the boiler combustor; and development of new types of packings and liquid distributors can be used for substantial reduction of the steam consumption of the method on the basis of a significant increase of the SO_2 concentration in the saturated absorbent and consequently enhancements of Wellman-Lord method. In wet FGD systems, lime is easier to manage on-site and has control efficiencies up to 95% but is significantly more costly; whereas, limestone is very inexpensive but control efficiencies for limestone systems are limited to approximately 90%. Generally, SO_2 control efficiencies for spray dry scrubbers are between 80% and 90%. Large units may require multiple absorber systems. The capital and annual costs for dry scrubbers are significantly lower than for wet scrubbers. Dry systems are installed easily and are good candidates for retrofit applications. SO_2 removal efficiencies are between 50% and 60% for calcium based sorbents and up to 80 % for sodium based sorbents injection into the duct and newer designs of dry systems for small industrial boilers have achieved greater than 90% SO_2 removal efficiencies.

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